U.S. Army Research, Development and Engineering Command

Laser-induced plasma chemistry of the explosive RDX with various metals

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TECHNOLOGY DRIVEN. WARFIGHTER FOCUSED.

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Outline

Motivation	Understand chemistry between metal nanoparticles and molecular explosives	Develop more efficient explosives
LIBS	Nanoparticle production followed by laser-induced plasma chemistry	Time-resolved emission spectra
Laser Parameters	Laser pulse energy dependence	Single vs. double pulse
Substrate characterization	Matrix effects	Effect of impurities on chemistry
Experiments	Double pulse (air/argon)	Aluminum powder additives
RDX discrimination	RDX residue on various metals	Effects of substrate on discrimination

Motivation

IOP Publishing — Journal of Physics D: Applied Physics
J. Phys. D: Appl. Phys. 40 (2007) 3541–3544 — doi:10.1088/0022-3727/40/11/043

Optical investigation of shock-produced chemical products in pseudo-aluminized explosive powders explosion

Ye Song[1,2], Wu Jing-he[1,2], Wang Yan-ping[2], Wu Guo-dong[2] and Yang Xiang-dong[1,3]

[1] Institute of Atomic and Molecular Physics, Sichuan University, Chengdu 610065, People's Republic of China
[2] National Key Laboratory for Shock Wave and Detonation Physics Research, Institute of Fluid Physics, China Academy of Engineering Physics, Mianyang 621900, People's Republic of China

Investigated formation of carbon in aluminized-RDX shock tube initiation

Production of AlO and C decreases rocket propellant performance

- XRD confirmed presence of C and Al_2O_3 in blast residue

Observed that ↑ micron-Al results in ↑ C_2 emission

- AlO and C_2 emission collected with two 2-nm resolution monochrometers/PMTs

Our idea was to use Al nanoparticles rather than conventional micron-sized Al and look at the emission from additional atomic and molecular species, all on a much smaller scale

Methodology

- In the past decade, laser ablation has increasingly been used to produce metallic nanoparticles
  - the size and distribution of the nanoparticles can be controlled by:
    - sequential laser pulses, varying repetition rates
    - laser fluence, wavelength and pulse width
    - carrier gas (air, argon, nitrogen, etc.)

J. Laser Micro. Nanoengineer., 3(2), 100-105 (2008).

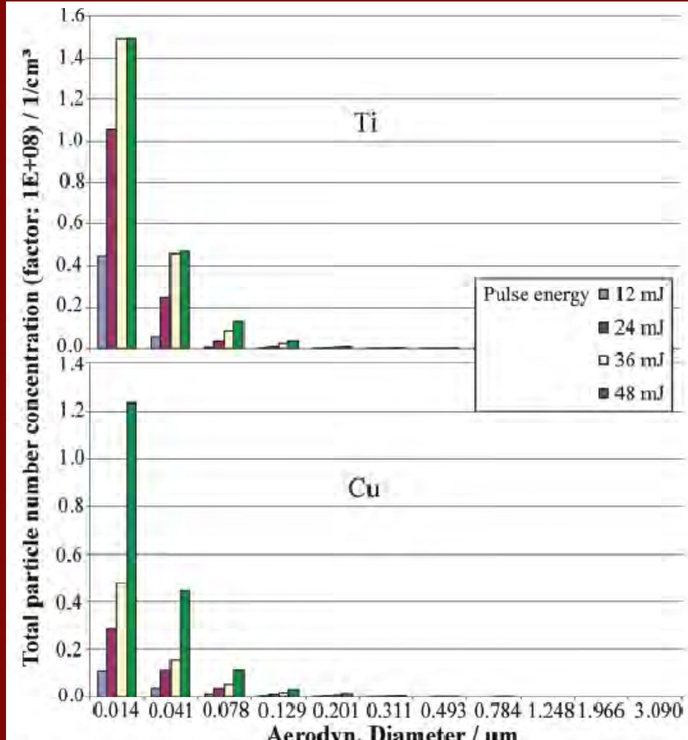

Fig. 3 Influence of the pulse energy on the particle size distribution of metal nanoparticles (carrier gas: N_2, gas pressure inside the chamber: 200kPa, pressure of the particle flow rate: 75kPa)

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Methodology

Key advantages of LIBS over the technique used by Song et al.:

Little or no sample preparation is needed

- no need to cast explosive formulations
- any type of material can be ablated with the laser as long as the laser energy > breakdown threshold

The properties of the laser (pulse energy, wavelength, pulse duration) can be tuned to control the size of the particles formed

- laser-generated nanoparticle formation

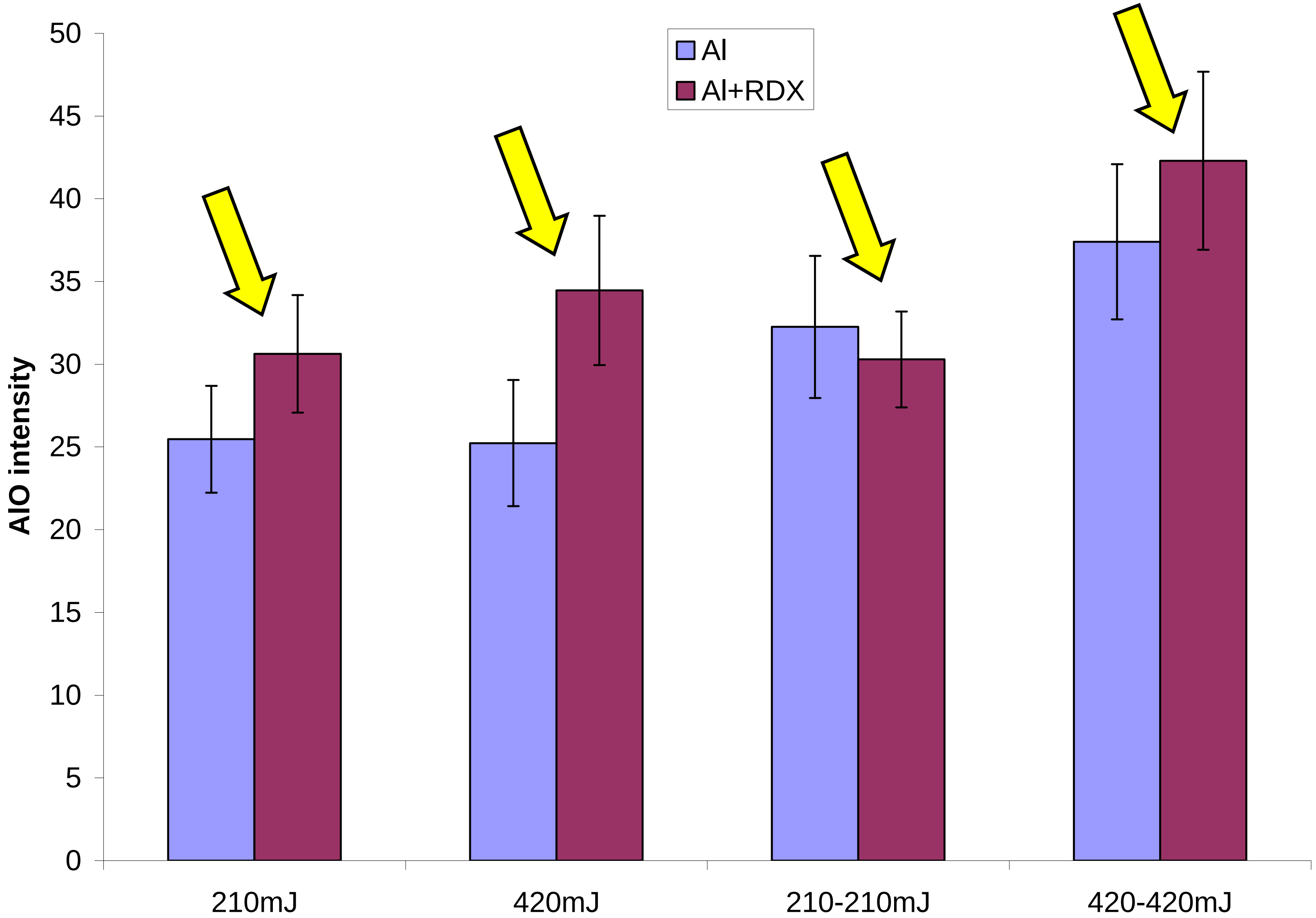
The intermediate chemical reactions of RDX and Al can be studied on a smaller scale

- no shock tube needed

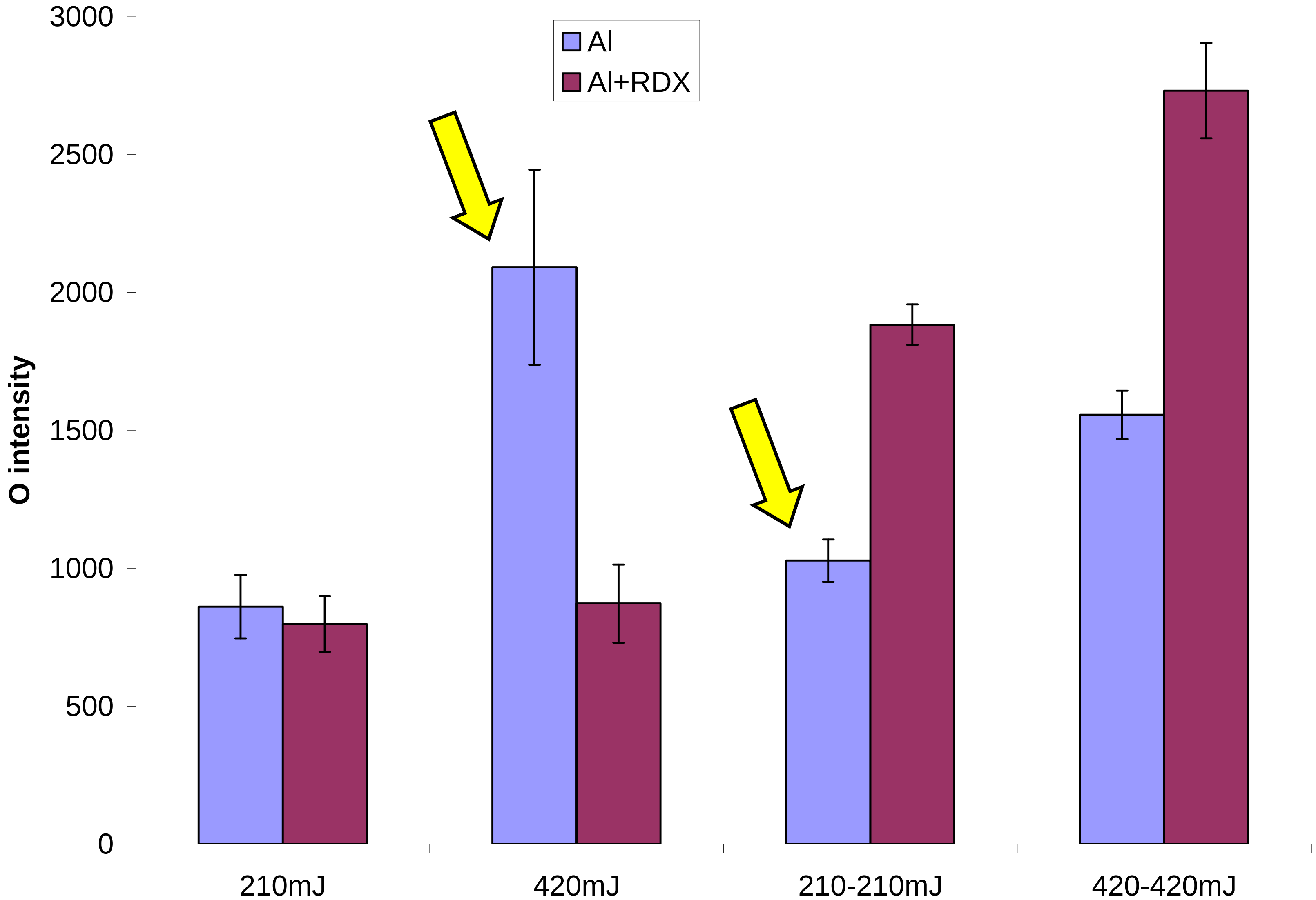
Ability to track relative concentrations of a large number of atomic and molecular species simultaneously

- $C + C \rightarrow C_2$
- $C + O_2 \rightarrow CO + O$, $CO + O \rightarrow CO_2$, $Al + CO_2 \rightarrow AlO + CO$
- also H, N, CN

Laser pulse energy studies



Laser pulse energy studies



Survey of Substrates

Question: do trace impurities in the metal substrate affect the plasma chemistry?

Spectra of 68 metal substrates were acquired

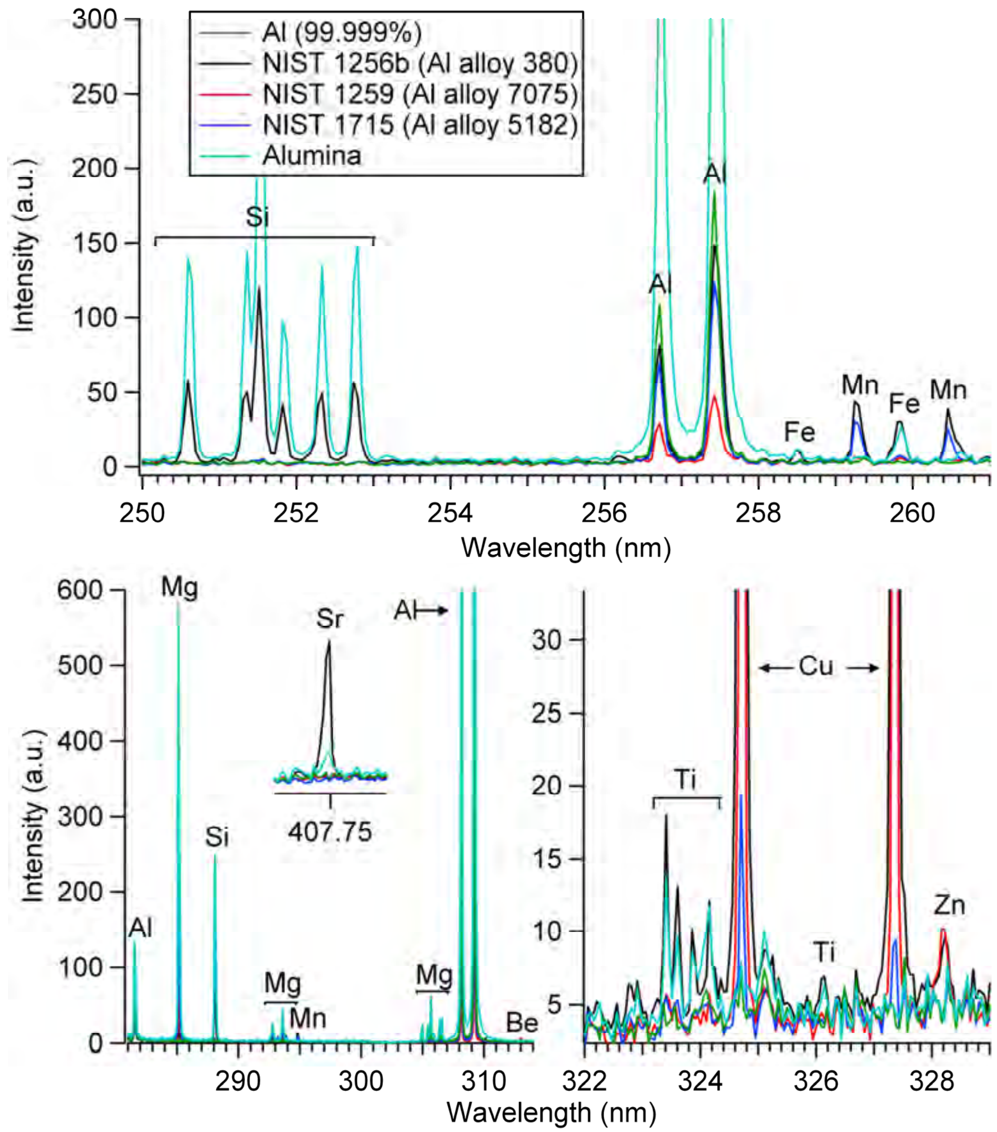
Samples surveyed included:

- high-purity aluminum (99.999%), copper (99.999%), nickel (99.98%), tin (99.998%) and titanium (99.998%)
- numerous metal alloys including brass, lead and steel

Differences in the spectra were observed based on trace element additives and impurities

Aluminum Alloys

- **Alumina (Al_2O_3)**
- **NIST 1256b (82.99%)**
  - 9.362% Si (obs.), 3.478% Cu (obs.), 1.011% Zn (obs.)
  - <1% Fe, Mn, Ni, Sn, Sr, Ti (obs.)
  - <0.1% Cr, Mg, Pb, V (not obs.)
- **NIST 1259 (89.76%)**
  - 5.44% Zn (obs.), 2.48% Mg (obs.), 1.60% Cu (obs.), 0.025% Be (obs.)
  - <0.2% Cr, Fe, Mn, Ni, Si (not obs.)
- **NIST 1715 (94.58%)**
  - 4.474% Mg (obs.), 0.3753% Mn (obs.)
  - <0.1% Cr, Cu, Fe, Ni, Pb, Si, Sr, Ti, V, Zn (not obs.)
- **Aluminum (99.999%)**



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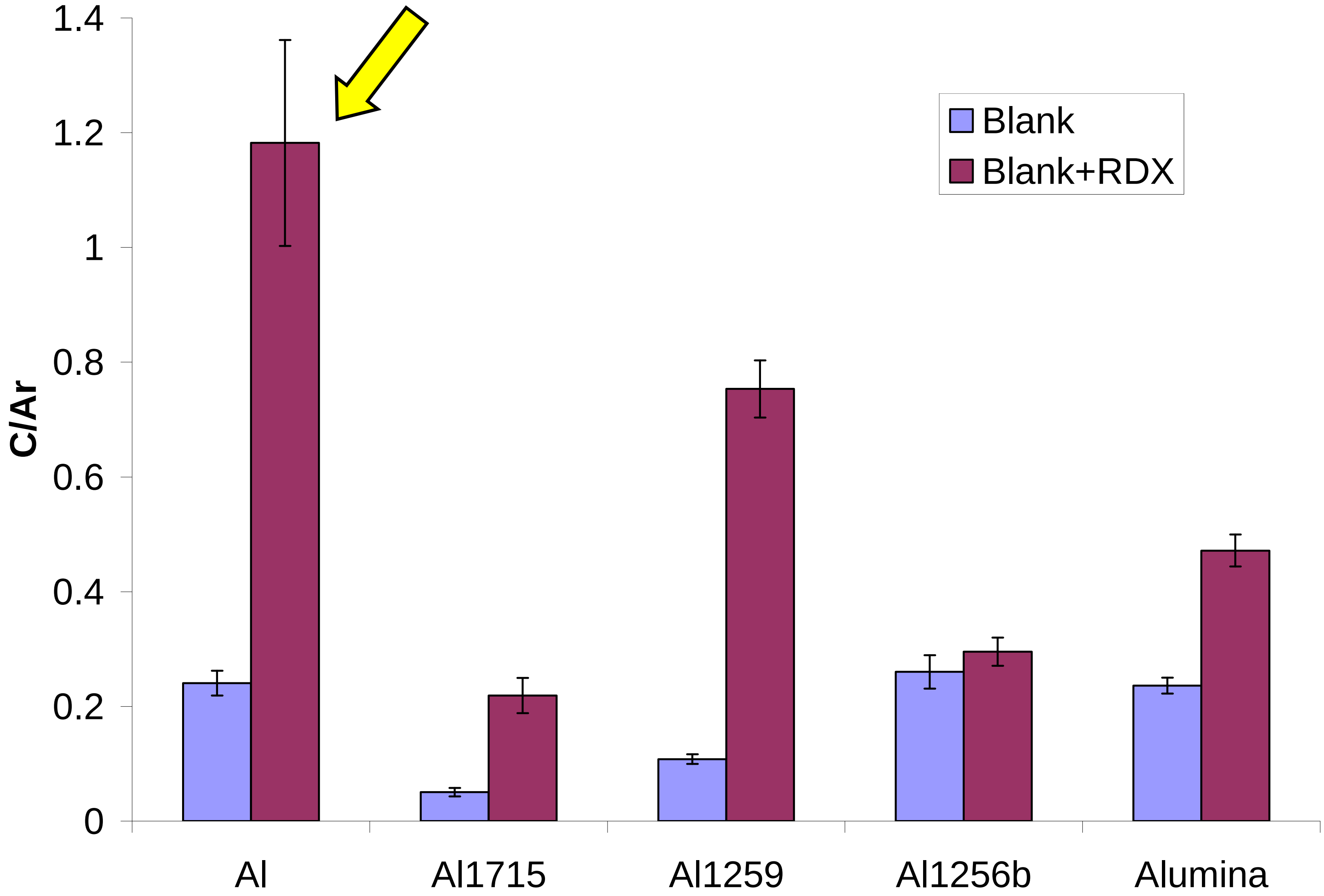
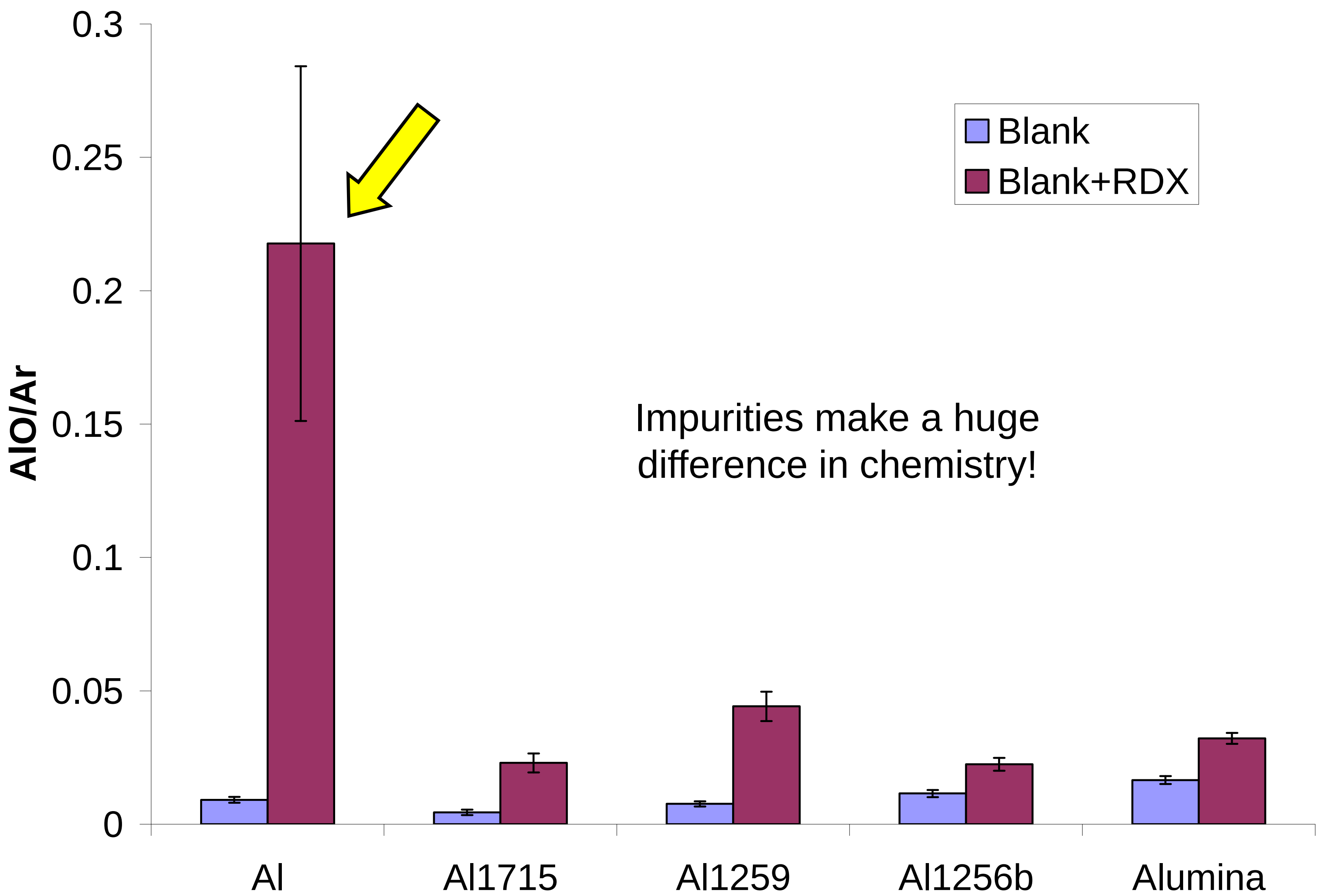
Aluminum – C signal



Aluminum – AlO signal



Double pulse experiments

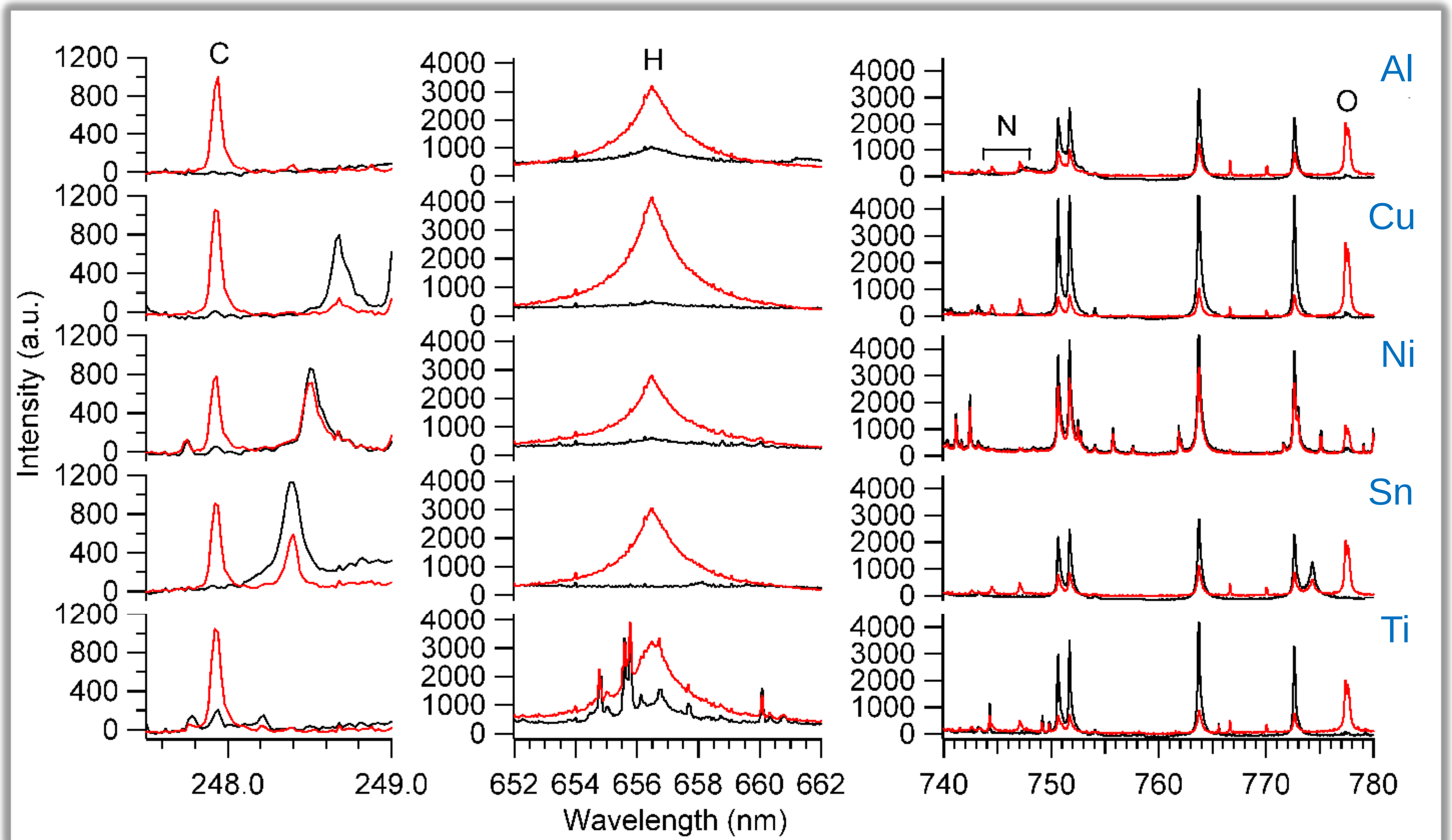
Double-pulse spectra acquired using a Continuum Surelite two-laser system w/echelle spectrograph (EMU-65 with an EMCCD camera)

- 420 mJ per laser, $\Delta t=2\mu s$, $t_{delay}=1.0\mu s$, $t_{gate}=50\mu s$

Spectra of 5 substrates with and without RDX residue were obtained in air and under an argon flow

- Al (99.999%), Cu (99.999%), Ni (99.98%), Sn (99.998%), and Ti (99.7%)

Double pulse spectra (argon)



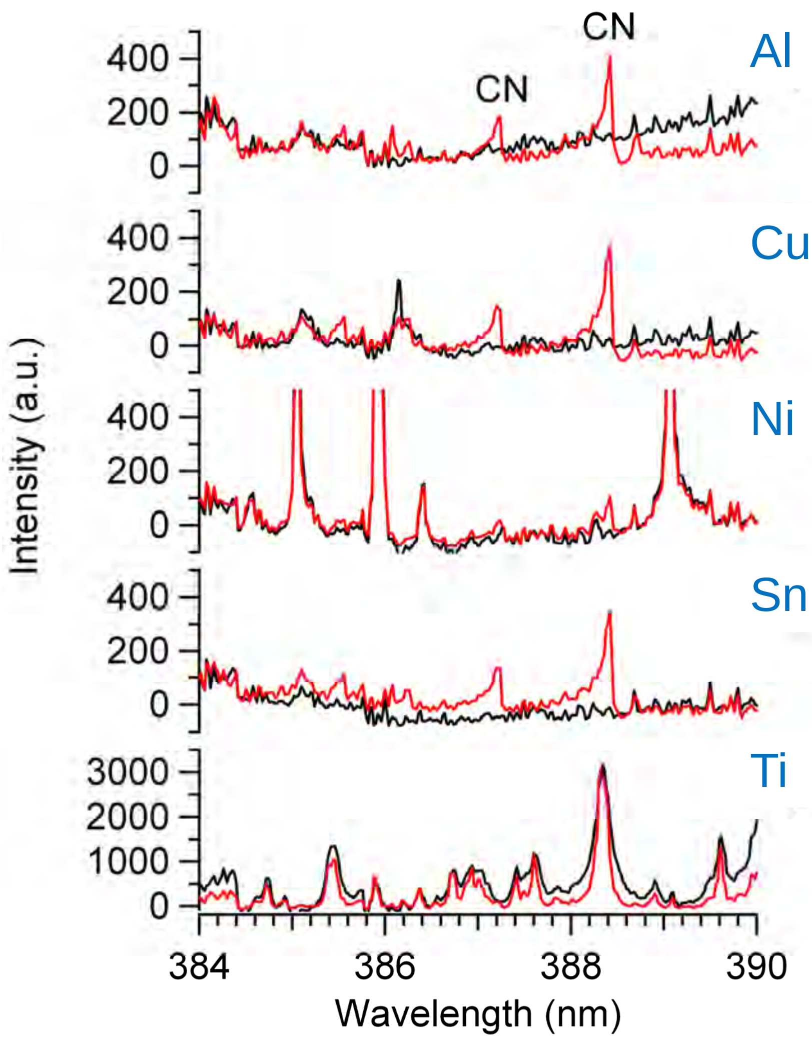
Double pulse spectra (argon)

V.I. Babushok, F.C. DeLucia, P.J. Dagdigian, J.L. Gottfried et al., Kinetic modeling study of the laser-induced plasma plume of cyclotrimethylenetrinitramine (RDX), *Spectrochim. Acta, Part B*, **62B**, 1321-1328 (2007).

- the nitrogen must come from the explosive when under argon
- therefore the CN formation is indicative of the chemical reactions the RDX undergoes in the plasma

$$C + N_2 \rightarrow CN + N$$

$$C_2 + N_2 \rightarrow 2\ CN$$

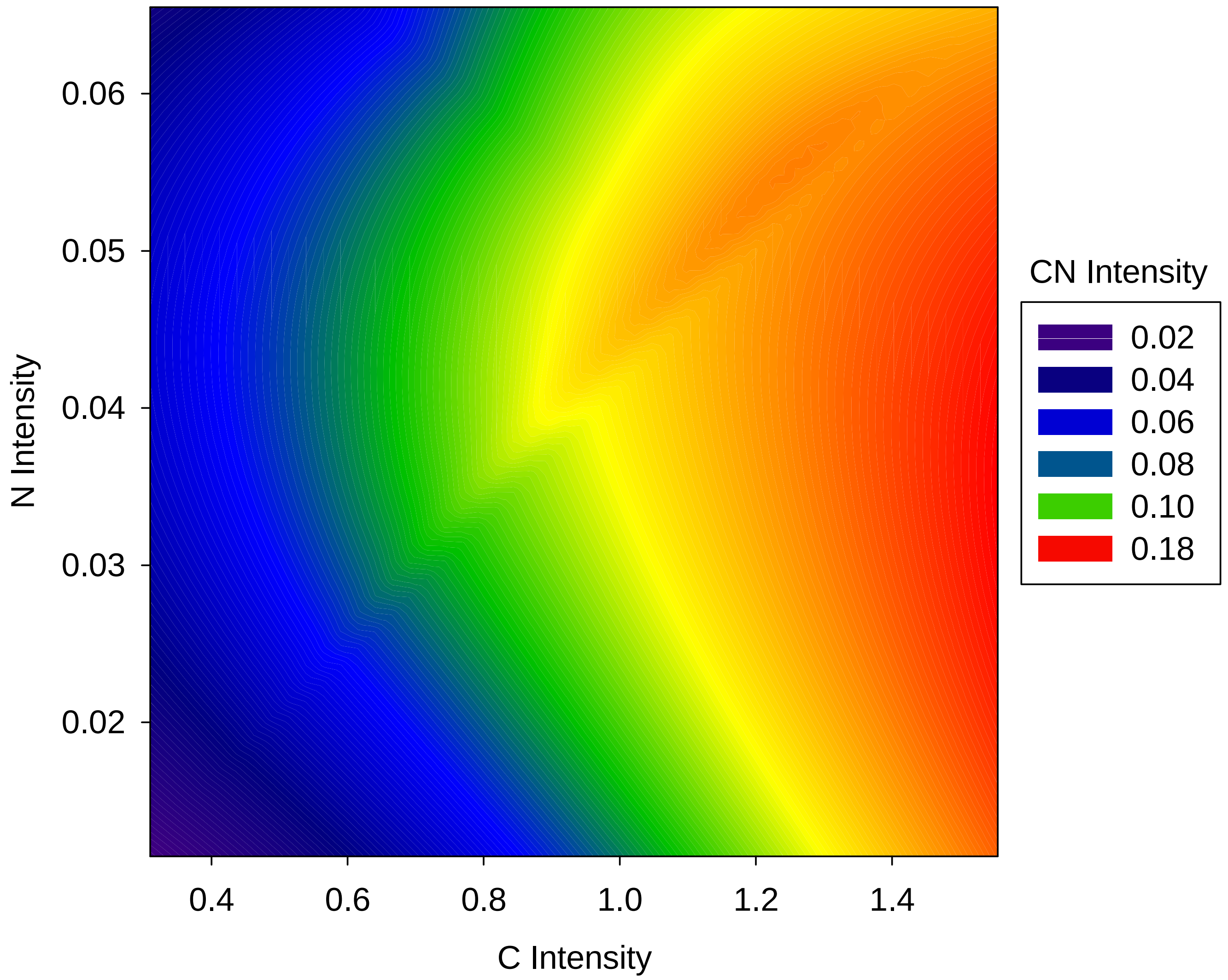


Double pulse results (argon)

$C+N_2 \rightarrow CN+N$

$C_2+N_2 \rightarrow 2\,CN$

$C+N+M \rightarrow CN+M$

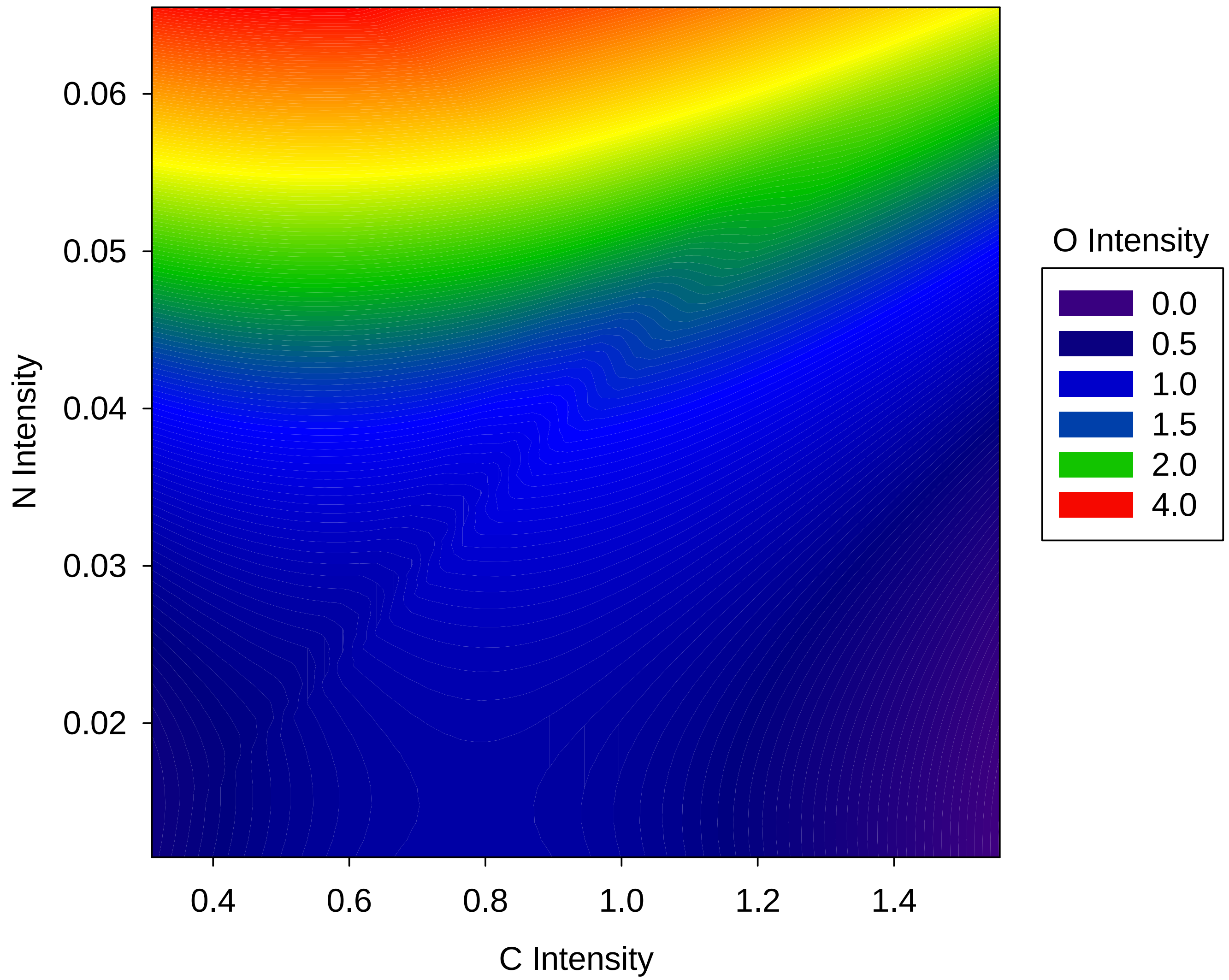


Double pulse results (argon)

$C+O+M \rightarrow CO+M$

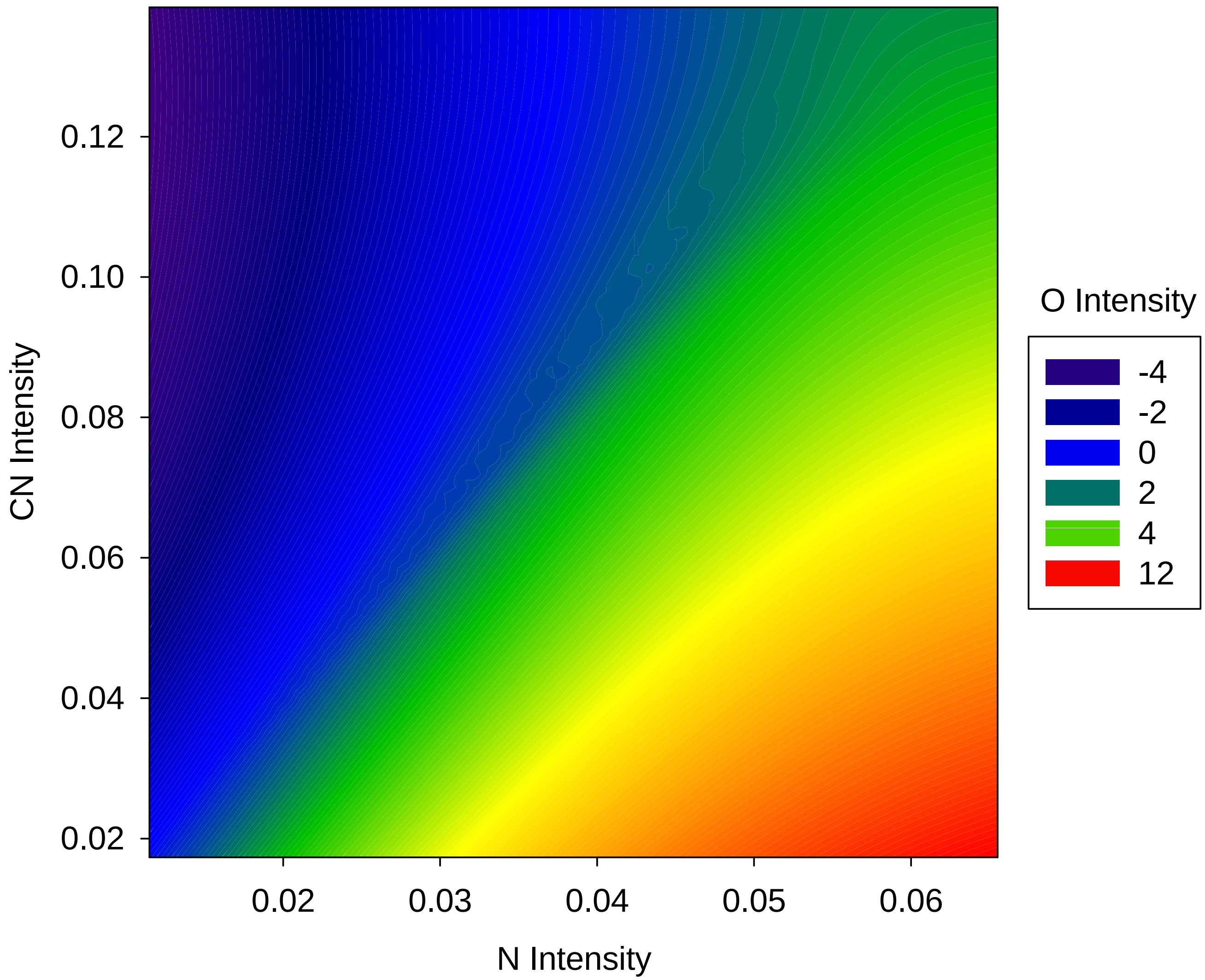
$C+O_2 \rightarrow CO+O$

$CO+O \rightarrow CO_2$



Double pulse results (argon)

CN+O → CO+N



Aluminum powder additive

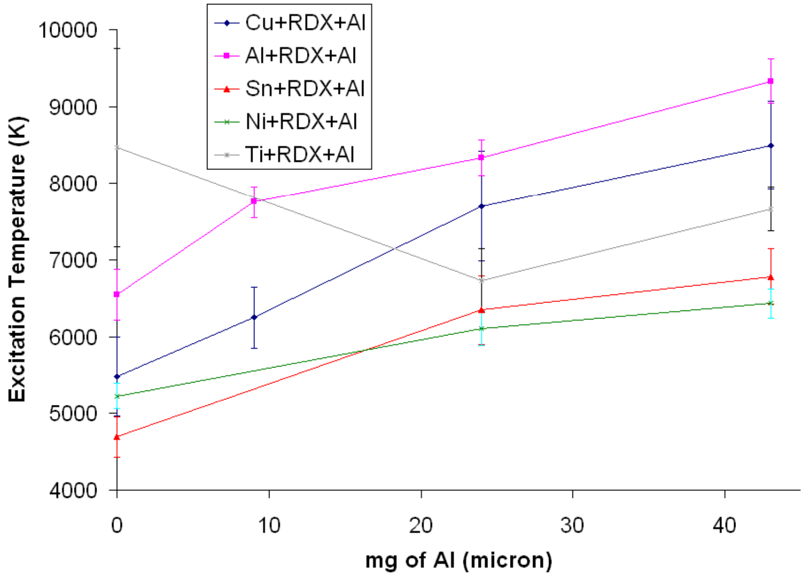
<75 µm Al powder mixed with RDX in varying concentrations

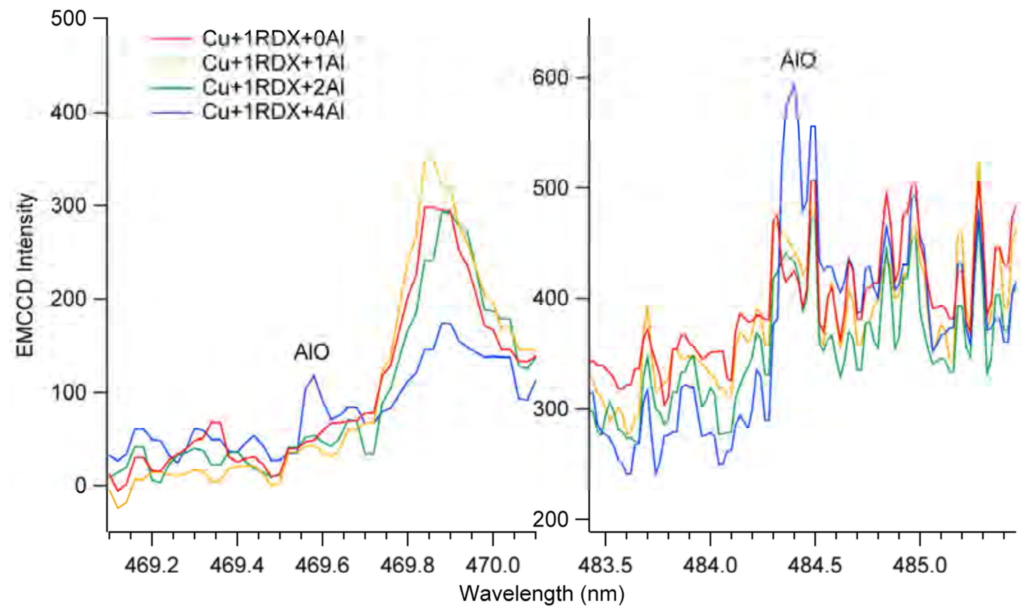
- 1:0, 1:1, 1:2, and 1:4 RDX to Al mixtures
- substrates: Al, Cu, Ni, Sn, and Ti
- double pulse laser system under argon

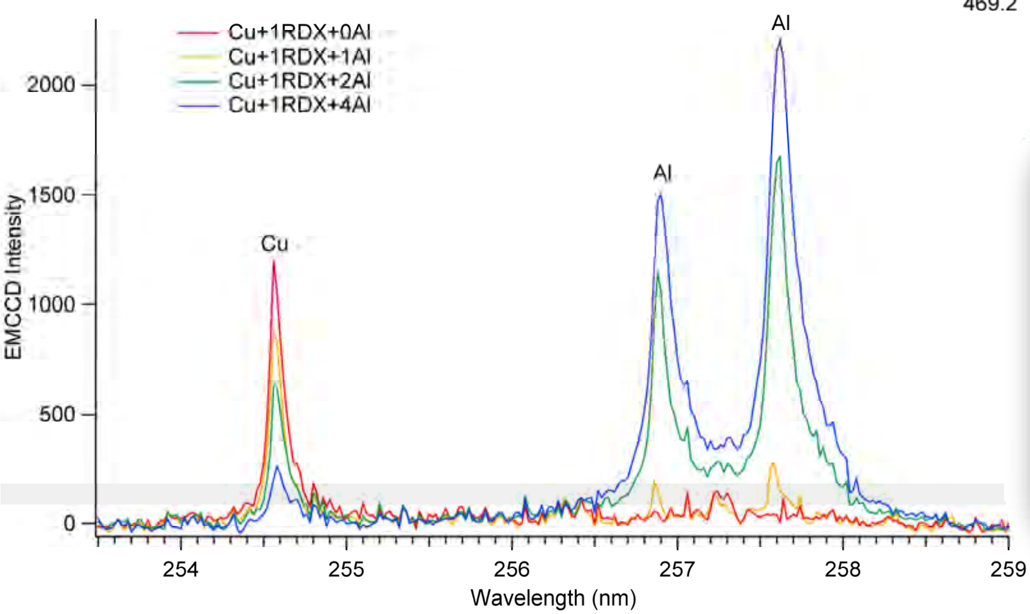
RDX/Al mixtures were crushed onto the substrate surfaces

- each laser shot would blow off a significant amount of material
- 15 spectra of each sample were acquired

Aluminum powder additive

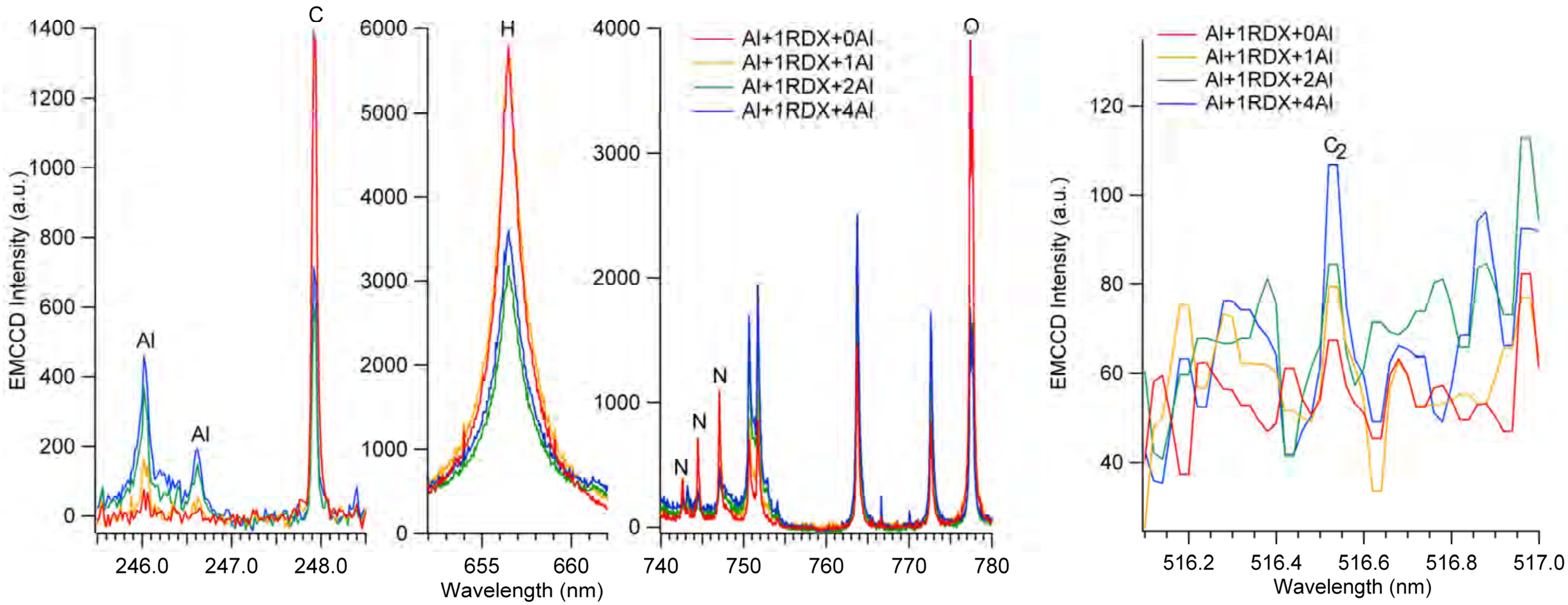






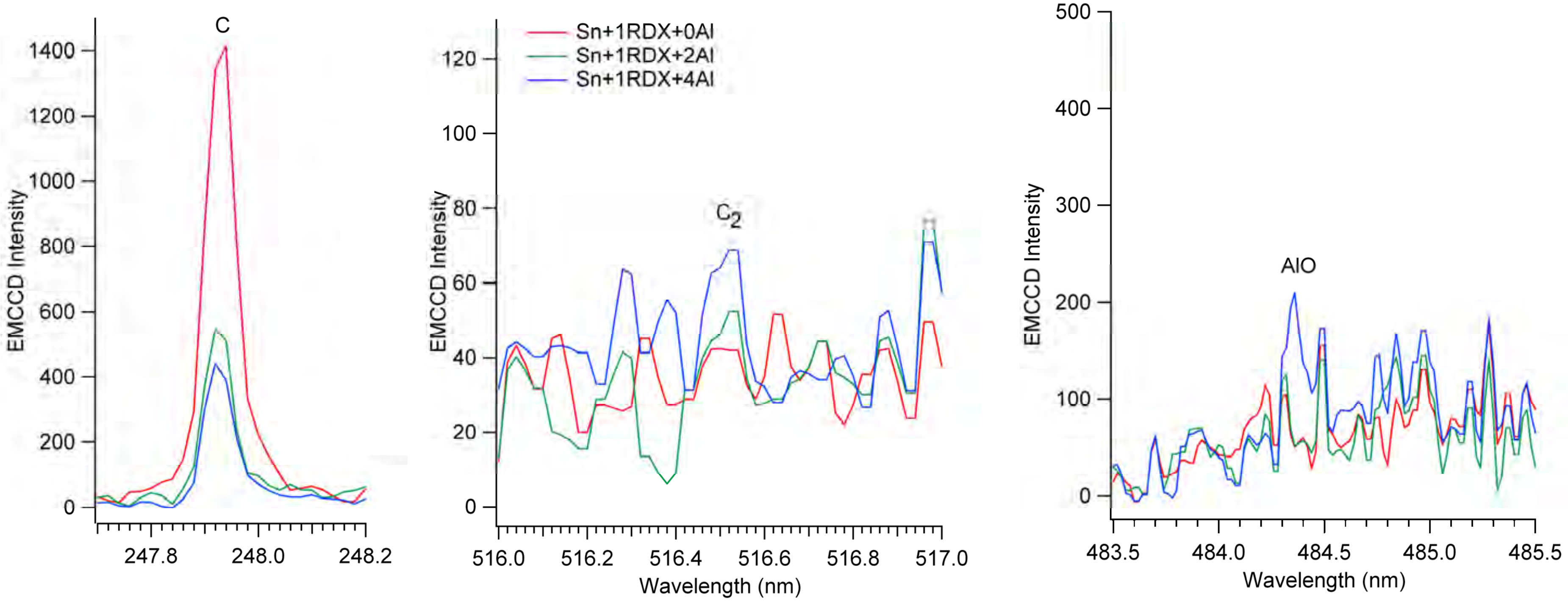
- increasing the Al:
  - – ↑ T_{exc}
  - – ↓ substrate emission
  - – ↑ Al emission
  - – ↑ AlO emission

Aluminum powder additive



- increasing the Al:
  - ↓ C, H, N, O and CN emission (less RDX sampled?)
  - ↑ C_2 emission (O being scavenged by the Al, less CO and CO_2)

Aluminum powder additive



- same optical emission trends observed on all 5 substrates (Al, Cu, Ni, Sn, and Ti)
- ↑ C_2 and AlO confirms observations of Song et al.!
  - decrease in atomic C is new information

Classification of RDX on metals

PLS-DA model: 11 classes of pure metals with and without RDX

- RDX+(Al, Cu, Ni, Sn, Ti, Au, Mg, Zn, In, Ag) = 1 class
- Al, Cu, Ni, Sn, Ti, Au, Mg, Zn, In, Ag
- 20 latent variables

Test samples: additional spectra from each sample type

- 400 spectra in test set

Test samples: spectra acquired on metal alloys not in model

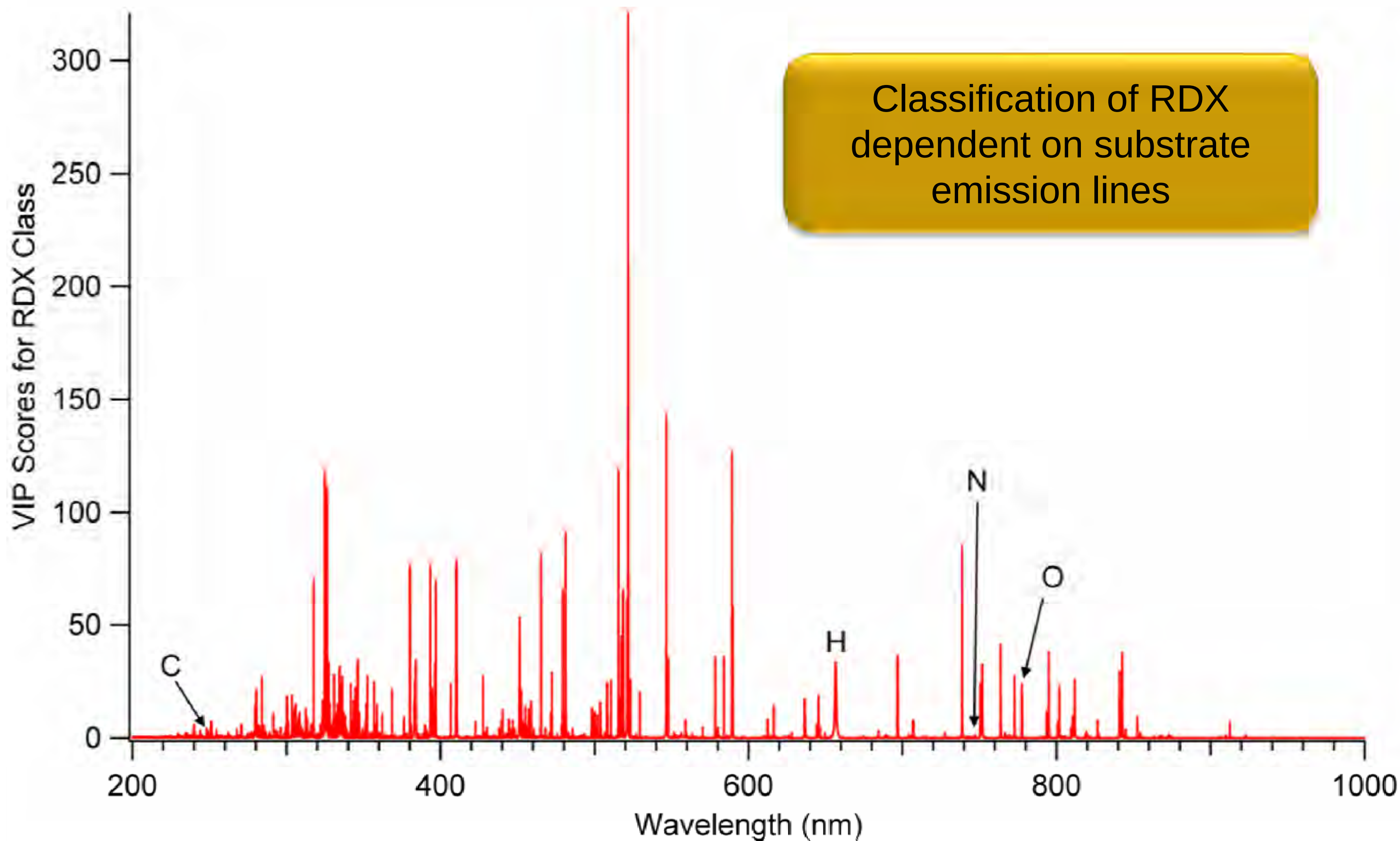
- 160 spectra in aluminum alloy test set
- 280 spectra in other metal alloy test set

Classification of RDX on metals

92.5% true positives, 2.5% false positives

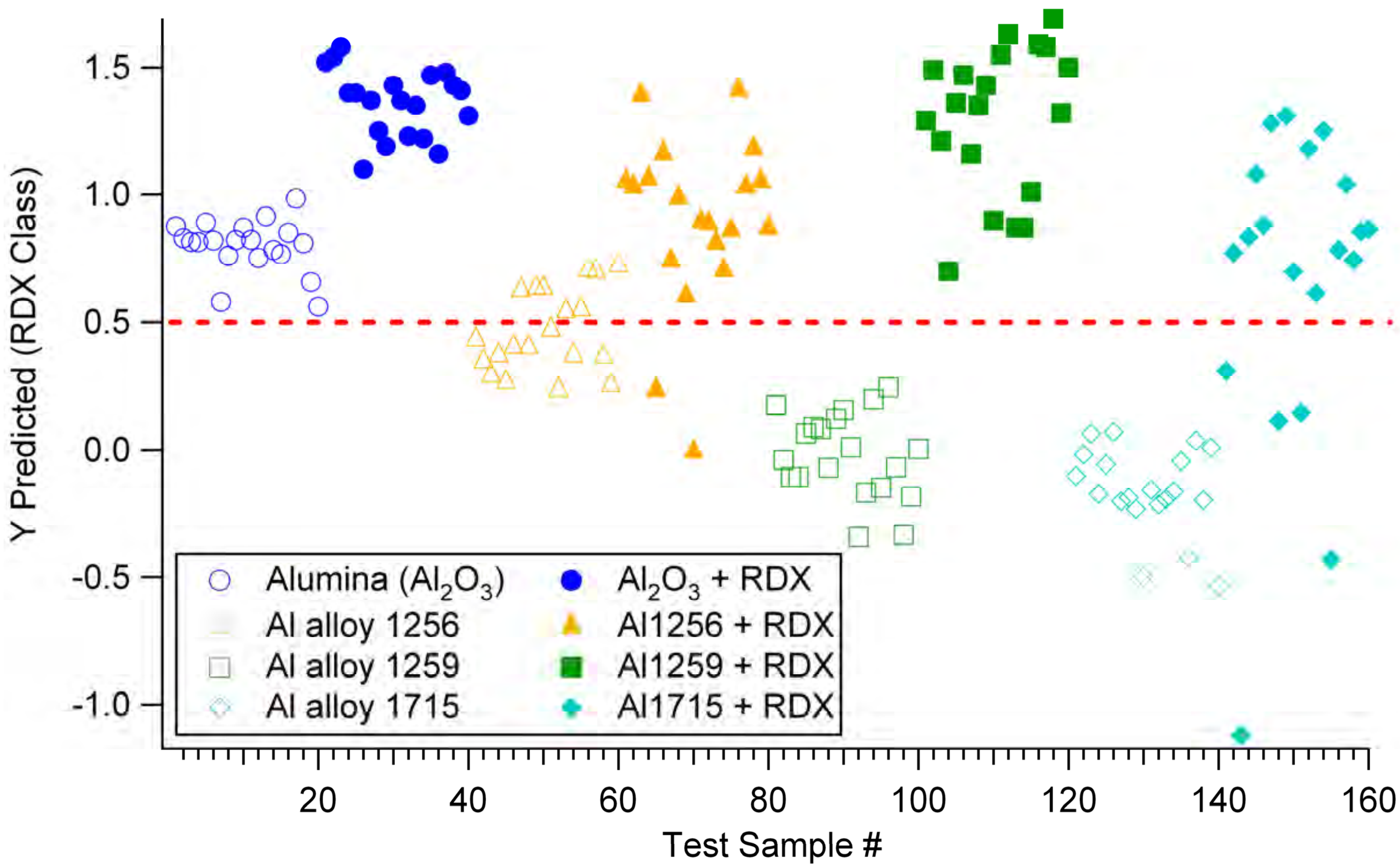
	RDX	Ag	Al	Au	Cu	In	Mg	Ni	Sn	Ti	Zn
Al+RDX (35)	34	0	5	0	0	0	0	0	0	0	0
Cu+RDX (35)	35	0	0	0	1	0	0	0	0	0	0
Ni+RDX (35)	28	0	0	0	0	0	0	33	0	0	0
Sn+RDX (35)	31	0	0	1	0	0	3	0	0	0	0
Ti+RDX (35)	35	0	0	0	0	0	0	4	0	1	0
Au+RDX (5)	4	0	0	3	0	0	0	0	0	0	0
Mg+RDX (5)	5	0	0	0	0	0	4	0	0	0	0
Zn+RDX (5)	5	0	0	0	0	0	0	0	0	0	1
Ag+RDX (5)	5	0	0	0	0	0	0	0	0	0	0
In+RDX (5)	3	0	0	0	0	3	0	0	0	0	0
Ag (5)	0	5	0	0	0	0	0	0	0	0	0
Al (35)	0	0	35	0	0	0	0	0	0	0	0
Au (5)	0	0	0	5	0	0	0	0	0	0	0
Cu (35)	0	0	0	0	35	0	0	0	0	0	0
In (5)	2	0	0	0	0	4	0	0	0	0	0
Mg (5)	1	0	0	0	0	0	5	0	0	0	0
Ni (35)	2	0	0	0	0	0	0	34	0	0	0
Sn (35)	0	1	0	0	0	0	0	0	35	0	0
Ti (35)	0	0	0	0	0	0	0	0	0	35	0
Zn (5)	0	0	0	0	0	0	0	0	0	0	5

Classification of RDX on metals



Classification of RDX dependent on substrate emission lines

Classification of RDX on Al alloys (not in model)



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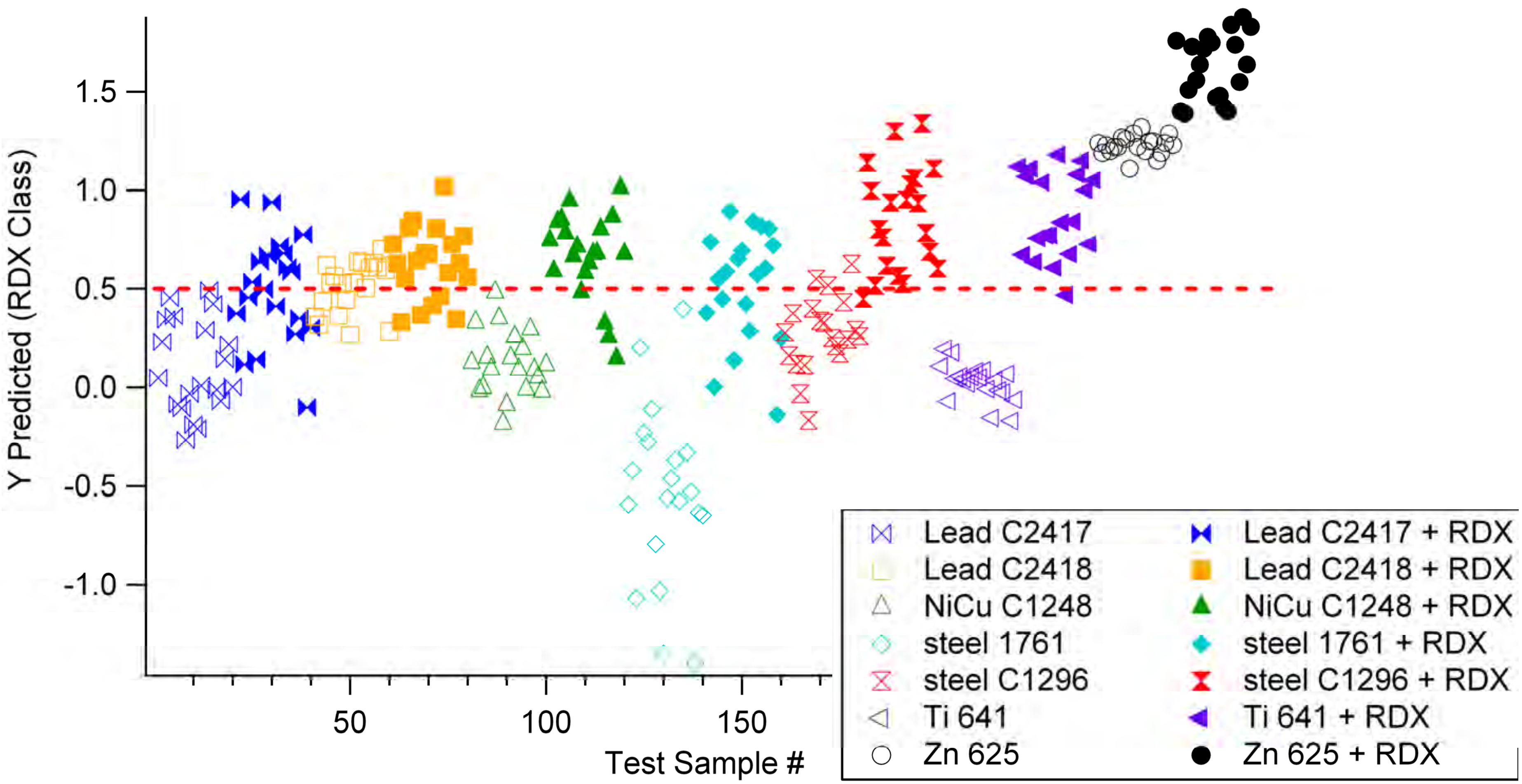
Classification of RDX on other alloys (not in model)



Conclusions

Time-resolved, broadband emission of chemical species involved in the reaction of RDX and Al were observed

Confirmed observations of Song et al. using the new experimental methodology	• plasma chemistry vs. shock tube detonation
Compared pure metal vs. alloys	• trace metals do affect chemistry, so broadband emission detection is extremely important
Demonstrated that laser pulse energy affects chemistry	• related to size of laser ablated particles

Despite differences in the plasma chemistry, RDX residue on different metal substrates can be correctly classified with PLS-DA